

THE CHEMISTRY OF ATOMIC CARBON

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A decade ago it was still said that the chemistry of atomic carbon was the first page of the book of organic chemistry, and that that page was blank. But even in the late forties and early fifties there were already some markings on the page.¹ The present rapid development of the field started about 1961 when it was proposed that the basic reaction mechanisms of atomic carbon with hydrocarbons was by insertion into C-H and C-C bonds.^{2,3} That blank first page is now quite well filled in as far as the basic outlines are concerned.⁴

The reason that the study of atomic carbon came so late is that this species is so reactive that it is difficult to produce in controlled conditions. Now, however, at least four techniques have been used: nuclear recoil⁴, photochemistry⁵, evaporation from graphite^{6,7,8}, and laser flash.⁹ Other methods have also been demonstrated but will not be reviewed here.

Nuclear Recoil Techniques

Nuclear recoil was the first technique used and it has supplied the bulk and the backbone of what we know at present of atomic carbon.⁴ Radioactive carbon is produced by a nuclear reaction. For instance on simply irradiating C^{12} with high energy gamma rays (> 20 Mev) the following process occurs



The C^{11} as initially produced may possess a very large amount of kinetic energy (~ 100 kev). This is lost in successive collisions. When the energy of the atom falls into the chemical energy range below 100 eV it may react to combine. Labelled molecules are formed by this means and may be assayed by radiogasschromotography.

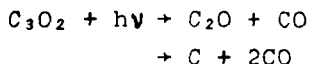
Considerations of atomic physics require, and experiment confirms, that as the carbon atoms reach the chemical energy range they are in a low-lying electronic state, either in 3P , 1D or 1S .^{10a,b} They may however react while they are still "hot",

i. e. have excess kinetic energy. This is rather an advantage, however, since one may control the energy of reaction by the use of moderators. In a system containing a large excess of a rare gas, essentially all reactions occur after the carbon atoms have been thermalized.

The nuclear method may be used with either C^{11} or C^{14} . However the half-life of C^{14} is so great that prolonged irradiation is required before enough is produced. This has led to serious difficulties with radiation damage effects. Most currently accepted data was obtained using C^{11} .

Photochemical Techniques

U.V. photolysis can be used to produce atomic carbon, e.g. with carbon suboxide.⁵



Atomic carbon is produced only if very short wave lengths ($\sim 1500 \text{ \AA}$) are used. This type of method has been employed both in the gas and solid phase. It is however severely restricted by the transparency of the medium to the needed radiation. For this reason methane is the only alkane whose reactions with atomic carbon have been studied by these means.

Evaporation Techniques

Several techniques have been developed in which carbon is evaporated from a heated graphite rod⁶, a carbon arc⁷, or an exploding filament⁸. The carbon vapor may be deposited on a surface on which it is allowed to react.

. This technique tends to be restricted to the study of reactions of atomic carbon on solid surfaces. The interpretation of gas-phase reactions would present difficulties because of extensive pyrolysis and photolysis on the evaporating body.

Laser Flash Techniques

We have recently developed⁹ a variant of the evaporation technique in which a laser is used. A pulse is focused onto a carbon surface forming a small hot spot from which carbon evaporates. Reactions with a low-pressure gas can be studied because the hot spot is so small and short lived that extensive pyrolysis does not occur.

While the use of a laser flash represents an advantage in that reactions in the gas phase can be treated it still shares

with other evaporation techniques, the disadvantage that a range of carbon species C_1 , C_2 , C_3 etc. are formed.

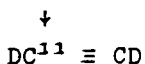
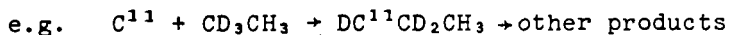
Comparison of Techniques

All techniques, though generally used under different conditions, tend to give very similar results in so far as a comparison can be made. However Skell has reported apparently significant differences in his evaporation techniques, which would tend to indicate that species of lower energy are involved⁷. In particular acetylene, a high energy product normally found when atomic carbon reacts with hydrocarbons is conspicuously absent when the particular method in question is used. This apparent discrepancy has not yet been resolved. One possible explanation¹⁰ stems from the fact that in this technique alone there is an appreciable delay between production and reaction of the carbon atoms. Conceivably this might allow complexing of the carbon atoms, reducing their reactivity, something that commonly happens to active species on aging in ordinary vacuums. Such complexed species could act as carbon atom donors, with reactions similar to but less energetic than those of free carbon atoms. Indeed a time dependence of reactivity is found in these experiments⁷, though this has been attributed to decay of spin states.

Summary of Findings

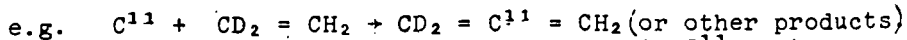
So much is now known of the reactions of atomic carbon that it is impossible to give a brief yet comprehensive review. Reactions with inorganic oxides¹¹, with nitrogen¹¹ and with hydrogen¹² are reviewed elsewhere. With hydrocarbons there are three principal modes of primary reactions.

1) Insertion into a C-H bond



As expected the acetylene formed in such reaction with CD_3CH_3 is either $C^{11}D \equiv CD$ or $C^{11}H \equiv CH$ with little $C^{11}D \equiv CH$ being formed^{4a}.

2) Insertion into a C = C bond



As expected the allene formed by this reaction is C^{11} center labeled and has the hydrogen isotope distribution shown.^{4a}

3) Abstraction to form CH_2



Primary modes 1) and 2) yield an intermediate adduct which is highly excited due to the energy released in forming

the new bonds. The further fate of such complexes depends on their spin states and on how rapidly energy is moved by collisional deactivation. This topic is well understood and is fully discussed elsewhere.^{13,14}

Insertion in C-C and C-F bonds has not been observed. Instead in perfluorocarbons the dominant reaction appears to be abstraction to form C-F, fluoromethyne.⁹ The probable explanation for this pattern of primary insertion will be discussed.

Acknowledgement

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- References -

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